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Detection of Metastable Atoms and Molecules using Rare-Gas Matrices

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I. Introduction.

Metastable atoms and molecules play an important role in a variety of situations ranging from electrical discharges to astrophysical phenomena [see e.g. G.S. Khromov, (1965), Borcia et al (2011), Nikolic et al (2012)]. They can influence biological situations as well. They have been observed to moderate bio-chemical reactions and may play a role in regenerating nerve tissue [Rochkind and Ouaknine, (1992)]. The damaging effects of sunlight on many organic materials (polymers, etc.) are often attributed to the effects of metastable oxygen while in photodynamic therapy, metastable oxygen is produced to kill cancer cells [Chen et al (2002)]. Han et al (2013) have used a metastable-rich atmospheric plasma jet to study DNA damage in oral cancer cells. While most atoms and molecules have metastable states, we will be concentrating in this report on those atoms, like oxygen and sulfur, which possess an np^4 electron configuration in the ground state. These species have proved to be detectable using the rare-gas matrix technique. For convenience we give a simplified energy level diagram of atomic oxygen in Figure 1.

![Energy Level Diagram](image)

Figure 1. Simplified term diagram for atomic oxygen. Note the “forbidden” transitions within the ground 2p^4 configuration. Adapted from McConkey et al (2008).
Metastable oxygen atoms are important constituents of the terrestrial atmosphere [Rees (1989)] where the well known ‘nebular’ red lines at 630 and 636.4 nm in the airglow and auroral spectra result from O(1D – 3P) decay and the ‘auroral’ and ‘transauroral’ lines at 557.7, 297.2 and 295.8 nm are due to the decay of O(1S) to O(1D) and O(3P). Both the intensity and polarization of these lines have proved to be significant [Lilensten et al, (2008), Bommier et al, (2011)]. A major source of metastable oxygen atoms in the atmosphere is photo-dissociation of O$_2$ or O$_3$ by solar ultraviolet photons. These atoms play a vital role in earth’s atmosphere through quenching processes, which lead to heating, and chemical reactions which modify its chemical composition, particularly in the stratosphere [Rees (1989), Kharchenko et al (2005), Vranckx et al (2010)]. Beyond earth’s environment, O(1D) is an active participant in cometary processes [Bhardwaj and Haider, (2002)].

Because these metastables have excited states where no electric dipole transition path to a lower state is possible, they must decay either collisionally or via magnetic dipole or electric quadrupole transitions. Because such transition probabilities are very low the metastable atoms or molecules normally have very long lifetimes, often more than a million times longer than regular excited states. This long lifetime is what makes their detection difficult in the laboratory. Wall or collisional quenching occurs long before a countable photon is emitted. Use of the rare-gas matrix method allows the lifetime to be shortened by many orders of magnitude (10$^7$ in the case of O(1S)).

II.A Relevant Background.

Previous attempts to detect O(1S) by techniques such as Auger emission from a low work function surface [Gilpin and Welge, (1971), Allcock and McConkey (1978)], by a chemi-ionization process [Stone et al. (1976)], or by detection of inelastically scattered electrons, were limited by a lack of sensitivity or suffered from poor discrimination against other metastable atomic or molecular species, such as O(5S), or ground state O(3P), and generally suffered from poor signal to background ratios.
Optical methods to record emissions from the low lying oxygen metastables relied on buffering the metastable atoms from the walls using rare gases such as He, as used by McLennan and Shrum (1925) in their historic experiment or by lifetime shortening through excimer formation with high pressure Kr or Xe gases [Kenty et al (1946), Herman and Herman (1950), Cooper et al (1961), Cunningham and Clark (1974), Huestis et al (1975),Simmons et al (1979)]. Unfortunately, these indirect methods can not be used to obtain important information such as absolute excitation cross sections or kinetic energies released in the decay of the repulsive excited molecular states that produce the metastable atoms.

A breakthrough occurred with the development of the field of Matrix Isolation Spectroscopy. In 1948 Vegard and Kvfite realized that green line emission, observed when a small oxygen impurity was present in a solid N$_2$:Ar mixture, was due to the O($^1$S-$^1$D) transition. Later Schoen and Broida (1960) presented excimer spectra obtained when a small amount of oxygen was frozen in a rare gas matrix at a temperature of 4K and bombarded with energetic electrons. Yurtaeva et al (1990) obtained similar results. There have been many examples of this matrix isolation spectroscopy using both electron and photon bombardment [e.g. Goodman et al, (1977), Taylor et al, (1981), Walker et al, (1981), Maillard et al, (1982), Fournier et al, (1982), Maillard et al, (1983), Girardet et al, (1986), Lawrence and Apkarian, (1992), Belov et al, (2000), Belov and Yurtaeva, (2001)]. Figure 2, adapted from Schoen and Broida illustrates the oxygen excimer spectrum obtained when different rare gas hosts were used.

The fact that the O($^1$S) state lifetime was very much shorter, when it combined with Xe to form a XeO* excimer state, was investigated quantitatively by Goodman et al (1977). They found a lifetime of 112 ns for the XeO($2^1\Sigma^+$) state in an Ar matrix at 22K. This is about a factor of $10^7$ shorter than the free state lifetime of O($^1$S).

[Insert Figure 2 here]
Kiefl et al. (1983) were the first to apply these concepts to develop a single particle detector for O(1S). A schematic of their apparatus is shown in Figure 3. They used a pulsed electron impact source to produce O(1S) together with a novel detector consisting of a layer of Xe freshly deposited on a cryogenically cooled (70 K) surface. Electric fields applied between the source and detector prevented any charged particles or Rydberg particles from reaching the detector. Using a time-of-flight (TOF) technique they measured relative extinction cross sections for O(1S) in various gases but did not report any excitation cross sections.
Kiefl et al used a combination of edge filters to observe photons emitted from the Xe-coated cold finger with wavelengths between 500 and 600 nm. As can be seen from Figures 2 and 4 this is not the optimum range for detection of the XeO* excimer emissions. However their TOF and deduced kinetic energy data for O(^1S) production from O_2 was confirmed by later data [LeClair and McConkey, (1993)].

An initial attempt to detect O(^1S) in our laboratory [Corr (1987), Corr et al, (1988)] was unsuccessful because of a combination of experimental parameters. The electron source used was a tungsten filament which had a short lifetime particularly in an O_2 atmosphere. Also, available filters and photomultipliers limited detection of photons to the blue-green spectral region whereas the excimer emission occurs predominantly at higher wavelengths as shown later. However formation of metastable O^+(^2D) following dissociative ionization of O_2 was demonstrated. This will be discussed in Section VII. This preliminary experiment suggested some important necessary modifications and improvements to our experimental set-up. When these were incorporated we were not only able to observe and quantify O(^1S) production from a large number of oxygen-containing molecules but also to detect a number of other metastable species as well. This is discussed fully in the following sections.
II.B Principle of Operation of the detector.

We will discuss the operation of the detector using Xe as the sensitive surface but similar arguments will apply when the other rare gases are considered. First we consider the spectral output from the surface when O($^1S$) from N$_2$O targets are incident upon it. A low resolution uncalibrated spectrum is shown in Figure 4.

![Figure 4. Low resolution optical spectrum from the xenon layer using N$_2$O as the target gas. Note the factor of 5 magnification applied to the data below 600 nm. A smooth curve has been drawn through the data points to guide the eye. From LeClair (1993).](image)

We first note the weak emission in the green which explains why Kiefl et al (1983) were able to make the observations that they did. The other two features were at 375 nm and a much stronger emission centered at 725 nm. The most likely explanation of the observations was given by Lawrence and Apkarian (1992). They observed an emission spectrum very similar to that shown in Figure 4 following laser UV irradiation of solid Xe:N$_2$O mixtures. The explanation follows from the XeO Potential Energy diagram shown in Figure 5. Lawrence and Apkarian showed the existence of bound states with well developed minima within the solid matrix. They suggested that atomic oxygen, produced by N$_2$O dissociation, would find itself inserted at an interstitial site of octahedral symmetry in the solid Xe. From there excitation occurred to the ionic Xe$^+$O$^-$($3^1\Sigma^+$) state, about 5eV above the ground state, followed by relaxation to its potential minimum at about 4 eV. This minimum lies below the potential curve for the covalent XeO($2^1\Sigma^+$) state and, as a result, there is an avoided curve crossing. Transitions to the repulsive wall of the XeO($^1\Pi$) or to the potential minimum of the XeO($1^1\Sigma^+$) state gave rise to the observed near IR and near UV features respectively. Light production from the Xe detector in the current situation proceeds along the same lines only the upper state
is now populated by the O(1S₀) atoms inserted into the matrix following termination of their flight path.

Figure 5. XeO potential curves with the transitions seen in Fig 4. The dashed curves are from Dunning and Hay (1977) and Simmons et al (1979) while the solid curves are from Lawrence and Apkarian (1992). From LeClair and McConkey (1993)

III. Experimental Details.

III A. Time Of Flight (TOF) Spectroscopy.

Since metastable particles have long lifetimes, TOF spectroscopy offers an attractive technique to study them. By using a pulsed source and timing the arrival of particles at the detector, a TOF spectrum as shown in Figure 6 is obtained. The
speed, \( v \), of a particle is obtained directly and hence their kinetic energy, \( E = \frac{1}{2} mv^2 \), if the identity and hence mass, \( m \), of the particle is known. The kinetic energy distribution function, \( F(E) \), is obtained directly from the TOF distribution function, \( F(t) \) using the transformation (see e.g. Smyth et al (1973)):

\[
F(E) = t^3 F(t)/[md^2] 
\]  

(1)

where \( d \) is the length of the flight path. The \( t^3 \) factor in Equation 1 means that the signal due to lower kinetic energy particles (longer flight times) will be strongly enhanced when the transformation is carried out. Thus, TOF and kinetic energy spectra can look quite different with features being emphasized quite differently in each case (see LeClair and McConkey (1994) for an good example of this).

Figure 6. Synthetic TOF spectrum. Note the prompt photons coincident with the exciting electron beam pulse and the metastable spectrum at later times.

[Insert Figure 6 here]

If the lifetimes of the target states emitting photons in coincidence with the exciting electron pulse are very short then the “prompt” photon peak reflects the time variation of the electron pulse. If longer lived species are excited then a “tail” to the photon peak occurs which may overlap with part of the metastable spectrum. Ideally the exciting pulse should be as short as possible otherwise some “smearing out” of the metastable TOF distribution occurs. This can obscure structure in the distribution. If the electron pulse width is \( \Delta t \) and the zero of the TOF scale is taken at the centre of the electron pulse then the resulting smearing of the released kinetic energy (RKE) scale is given by:

\[
\Delta(RKE)/RKE = 2\Delta t/t \]  

(2)
Thus the broadening increases at short flight times. For example, LeClair and McConkey (1993) show O(\(^1\)S) TOF data from O\(_2\) targets which demonstrates that there is considerable signal at 25 µs where RKE = 18.8 eV. The uncertainty due to the 1 µs wide electron pulse is therefore ± 1.5 eV, but at 42 µs where the TOF spectra show a maximum, it is only ± 0.3 eV. Other factors which can affect the resolution of the TOF spectra have been discussed by Smyth et al (1973).

A particular TOF window corresponding to kinetic energies between \(E_1\) and \(E_2\), Figure 6, may be selected for further observation. By varying the electron impact energy, an “excitation function” for particles with kinetic energies in this range may be obtained.

### III B. Apparatus Details.

A schematic of the apparatus which was developed in our laboratory for these studies is shown in Figure 7. A number of points are critical to its optimum performance. These are stressed in the following section.

![Figure 7. Block diagram of the metastable atom detector system. A, amplifier; D, discriminator; P, pulser; F, filter; TP, turbopump; EG, electron gun; FC, Faraday](image-url)

[Insert Figure 7 here]
cup; MC, microwave cavity; BG, Baratron gauge; NV, needle valve; CG, convectron gauge; CF, cold finger; He, helium cryostat; RG, rare gas; De, deflector plates; FG, feed gas; MCS, multichannel scaler; PMT, photomultiplier tube. From Kedzierski et al (2010).

Differential pumping of the various vacuum components was critical. The electron gun housing was separately pumped as this greatly prolonged the lifetime of the electron source particularly when O$_2$ was being used as the target gas. In Corr’s preliminary experiment (Corr, (1987)) the tungsten filament was directly exposed to O$_2$ and only lasted for about eight hours. With differential pumping and also with replacement of the tungsten filament by a thoriated iridium one, filament lifetimes were extended to months rather than hours. Differential pumping of the flight path to the detector reduced the possibility of in-flight collisional loss of the metastable particles. The cold finger that formed the detector when coated with rare gas acted as an efficient cryopump for its chamber. Being in a separate chamber reduced the flow of rare gas required to maintain a fresh layer on the detector surface. Continuous refreshment of the detector surface was found to be essential. Without this, serious degradation of the surface occurred by background or target gases. The use of turbopumps enabled an oil-free environment to be maintained. In early experiments a container of liquid nitrogen boiling under reduced pressure, so that the cold finger could be cooled to 65 K, took the place of the He cryostat. At this temperature the vapour pressure of Xe was less than 3x10$^{-4}$ torr, LeClair(1993).

To reduce collisional loss of metastables in collisions with target gas molecules, the experiment was carried out in a crossed-beam mode. This enabled a high target density to be achieved but kept the background pressure low. Before introduction of the target gas beam the base pressure in the main chamber was 2 x 10$^{-7}$ Torr. When the beam was operational this pressure rose to the 10$^{-4}$-10$^{-5}$ Torr region.

Magnetic focusing of the electron gun was another essential factor as it enabled an electron beam of constant cross section and current to be achieved over a wide electron energy range. The magnetic field was provided by four Alnico-V magnetic rods, 1.5 cm in diameter and 15 cm long, clamped in a quadrupole arrangement as shown in Figure 8 with like poles at the same end. The magnetic field variation along the electron beam axis is also shown in Figure 8. Figure 9
shows a plot of integrated beam current versus electron beam energy when O₂ was being used as a target gas (10 torr upstream of the nozzle). It illustrates the very good characteristics of the gun. Two further advantages of the e-beam system should be noted. First, the open structure around the interaction allowed free passage of neutral products to the detector and second, the magnetic field had the effect of preventing charged particles from traversing to the detector region.

[Insert Figure 8 here]

Figure 8. Electron gun assembly. SR – support rods; FH – filament holder; EE – extraction electrode; CE – collimation electrode; CT – gas inlet capillary tube; IC – inner Faraday cup; OC – outer Faraday cup; MR – magnetic rod. The positions of the magnetic rods are partially drawn in with a light dashed line. The inset shows the orientation of the magnetic rods to the electrodes and the slits to the gas jet. The heavy dashed line represents the magnitude of the magnetic field along the electron beam axis, according to the scale on the right. From LeClair (1993).

Efficient detection of photons following excimer state decay was important also. In initial experiments we used a quartz lens system to focus light from the detector surface unto the photomultiplier tube cathode. This allowed detection over the entire wavelength range from 250nm to the infrared. This was important for certain studies where the excimer radiation occurred in the near UV, for example when detecting CO(a³Π), [LeClair and McConkey (1994), LeClair et al (1994)]. Appropriate filters could be used to isolate particular spectral regions or a mini monochromator could be used to survey the spectrum of light from the detector.
surface. In more recent versions of the apparatus a plexiglass light pipe was incorporated to boost the solid angle of detection and increase signal levels. This limited transmission to the visible and infrared regions.

[Insert Figure 9 here]

Figure 9. A plot of integrated current entering the inner Faraday cup as a function of electron impact energy. The inner cup was biased at +50V and the outer at +10V. Electron pulses were 20 µs long at a rate of 5 kHz. From LeClair (1993).

Pulses from the photomultiplier were processed by standard NIM electronics and used to stop a time to amplitude convertor (TAC) which had been started by a pulse from the experiment master oscillator. This master oscillator also supplied pulses to the electron gun pulser. The TAC output was fed to a pulse height analyser (PHA) so that a TOF spectrum was obtained. In more recent experiments the detector signals were handled by a SRI 430 multiscaler unit. Figure 10 shows a typical TOF spectrum.

[Insert Figure 10 here]
Figure 10. TOF spectrum following 100 eV electron impact on N\textsubscript{2}O. Electron pulses were 1 µs long. Note the prompt photon peak in the early channels coincident with the electron pulse. The peak around 50 µs comes from the arrival of O(\textsuperscript{1}S) atoms at the Xe surface. From LeClair (1993).

A plexiglass shutter (not shown in Figure 7) could be used to block the metastables from impacting the detector surface. This was useful especially when overlap occurred between the tail of the prompt photon peak and the metastable feature itself. The deflector plates, De on Figure 7, were not needed to prevent charged particles from reaching the detector as these were deflected by the magnetic field. They were however useful in quenching Rydberg particles and showing that these did not affect observed signals.

III.C. Apparatus Performance.

Spectral Output: The spectral output from a Xe matrix has been given in Figure 4 above. The main broad feature that involved decay of a XeO(\textsuperscript{1}S) excimer was centered on 725 nm. This work was extended by Kedzierski et al (2010) to include the other rare gas matrices. Their results are shown in Figure 11. Very similar data was demonstrated by Yurtaeva et al (1990) and we note the similarity to the earlier work where electron or photon bombardment of rare gas matrices containing a trace of oxygen occurred [Schoen and Broida (1960), Taylor et al (1981), Walker et al (1981)]. We note that only the main feature was considered in Figure 11. It
got progressively broader and moved to the red as the rare gas host was changed Ne to Ar to Kr to Xe. The different spectral outputs reflect the different excimer potential energy curves for the different rare gases.

Figure 11. Spectral output from the rare gas matrices as a function of wavelength. Target gas for production of \( \text{O}^\text{(1S)} \) was \( \text{N}_2\text{O} \) in each case and the e-beam energy was 100 eV. Solid lines (Gaussian curves) have been drawn through the experimental points which, except for the case of Xe, have been removed for the sake of clarity. All curves have been normalized to the same peak height. The data for the individual matrices are designated by the rare gas symbols at the peak of each curve. The temperature of the cold finger was 20K in each case. From Kedzierski et al (2010)

Insert Figure 11 here.

**Temperature Variation:** Figure 12 shows how the sensitivities of the different surfaces vary with the surface temperature. Again, The target gas for production of \( \text{O}^\text{(1S)} \) was \( \text{N}_2\text{O} \) in each case and the e-beam energy was 100 eV. For Xe this represents an extension of the earlier work of Kedzierski et al (1998) where data were limited to temperatures above 63K. For Kr we note the similarity between our data and those of Yurtaeva et al (1990). Figure 12 provides an estimate of the relative sensitivity of the different matrix surfaces. We note that in all cases the sensitivities rise as the cold finger temperature is reduced but tend to plateau (or even drop off slightly) at the lowest temperatures (<20K). It was noticed also that
the sensitivity tended to drop off after prolonged data taking periods. This is consistent with the thickening of the rare gas matrix on the cold finger which occurred as time progressed. As thickening occurs a rise in the surface temperature of the matrix results accompanied by a drop in sensitivity.

Work with RgO* emissions from rare gas matrices with small (~ 1%) content of an oxygen containing molecule and excitation with electron or photon bombardment reveals that the emissions were significantly affected by the temperature of the matrices [see e.g. Taylor et al (1981), Fugol’ et al (1986), Gudipati (1996), Danilychev and Apkarian (1993), Belov et al (2000)]. Fugol’ et al (1986) found a rapid drop in luminescence from their samples at temperatures above some critical temperature, somewhat similar to what we observe. They found critical temperatures of ~30K, ~30K and ~17K for Xe, Kr and Ar matrices respectively. They suggest that the phenomenon is related to the mobility of excitons within the crystal.

Figure 12. Variation of the sensitivity of the different matrices with cold finger temperature. Triangles, Kr; squares, Xe; circles, Ar; diamonds, Ne. Lines have been drawn through the experimental points to help guide the eye. Data are the average of a number of runs in each case and have been corrected for any variations in current and source pressure as well as for variations in the PMT quantum efficiency and length of data taking run. From Kedzierski et al (2010). Insert Figure 12 here.
Excimer Lifetimes: Kedzierski et al (2010) investigated how the excimer lifetimes varied with rare gas host by comparing the TOF spectra obtained using the different matrices. Their results are shown in Figure 13 obtained at an e-beam energy of 100 eV. N$_2$O is chosen as the target gas because it had been shown earlier [LeClair and McConkey (1993)] that a single dissociation channel dominated O($^1$S) production and also that no other metastable or Rydberg fragments from this target affected the detector when Xe was used. The data have not been normalized relative to one another. Note that the prompt photon peak has been suppressed for clarity for all the detector surfaces except xenon.

![Figure 13](image)

Figure 13. O($^1$S$_0$) TOF data for different rare gas matrices. Note that the data for the different matrices have not been normalized to one another. The individual data sets have been scaled so that differences are clearly visible. The e-beam energy was 100 eV in each case and the target was N$_2$O. The e-beam pulse width was 10 μs in each case. The cold finger temperature was ~17 K in each case. Note that the prompt photon peak starting at time zero has been suppressed for all the matrices except Xe for reasons of clarity.

Insert Figure 13 here.

We note that the basic shape of the TOF peak is the same for all surfaces except that a noticeable shift is evident in the case of argon. A likely explanation is that, with Ar, the excimer lifetime is more than 20 microseconds whereas with the other rare gases the lifetimes are much shorter. We may model the situation by
introducing an exponential factor, \( \exp[-t/\tau] \), where \( \tau \) represents the excimer lifetime. The modeling is based on the following equation:

\[
 f(t) = \int_{-\infty}^{t} f_{Xe}(t') \cdot \exp\left(-\left(t - t'\right)/\tau\right) \cdot dt'
\]  

(4)

Where \( f(t) \) defines the time evolution of the detected signal when a rare gas other than Xe is used, and \( f_{Xe}(t') \) is the time evolution of the detected signal from the XeO excimer. We find the lifetimes for Ne, Kr and Ar, which provide the best fit to the data, to be 0.2, 4.2 and 23.4 μs respectively. The lifetime of the XeO excimer is known to be about 200 ns [Lawrence and Apkarian (1992)] and thus is insignificant on the timescale of figure 13.

It is interesting to compare these lifetimes and those obtained from studies where rare gas matrices with small admixtures of oxygen-containing species were formed and then bombarded by either energetic electrons or photons. Thus Monaghan and Rehn (1978), using a 1% N\(_2\)O contaminant in Kr at a temperature of 25 K and bombarding with 9.5 eV photons from a pulsed synchrotron source, found KrO* lifetimes of 1.4 and 3.6 μs. The two lifetimes corresponded to transitions of slightly different energies (wavelengths) in the matrix. Danilychev and Apkarian (1993) found lifetimes of 1.4 and 11 μs for the same KrO* emissions. They assigned the two different transitions to O atoms isolated in different (interstitial and substitutional) lattice sites in the matrix. Taylor et al (1981) measured lifetimes of KrO* ranging from 0.5 to 1.5 μs when using 1% CO\(_2\) in a Kr matrix and bombarding with 11.05 eV photons. They found that the lifetime was affected by the temperature of the matrix. Taylor et al (1981) quote lifetime values of 40 and 20 μs for the ArO* emissions from an Ar matrix at a temperature lower than 17K with 1% N\(_2\)O content and 11 eV photon bombardment. The latter lifetime is in reasonable agreement with the 24μs obtained in the present work.

**IV. A. Calibration of O(\(^1\)S) production.**

The fact that production of O(\(^1\)S) from N\(_2\)O was shown by LeClair and McConkey (1993) to be completely dominated by a single repulsive state (\(D^1\Sigma^+\)) independent
of incident electron energy provided the basis for their absolute calibration
technique. The cross section for excitation of an optically allowed state \( i \) of an
atom or molecule, at sufficiently high energies that Bethe-Born theory (Bethe,
1930, Inokuti, 1971) is valid, is given by

\[
\sigma_i = \left[\frac{4\pi a_o^2}{E/R}\right] \cdot \left[\frac{f}{(E_i/R)}\right] \cdot \ln \left(\frac{4C_i E}{R}\right).
\]  

(IV A1)

Here \( E \) is the kinetic energy of the electrons, \( E_i \) the excitation energy of the state, \( f \)
the integrated optical oscillator strength of the transition, \( C_i \) is a constant dependent
on the transition, \( a_o \) is the radius of the first Bohr orbit, and \( R \) is the Rydberg
constant. A plot of \( \sigma E \) vs \( \ln E \) at high energy is a straight line whose slope is
related to \( f \) and whose intercept with the energy axis gives \( C_i \) directly, (see Figure
14).

![Bethe plot](image)

Figure 14. Bethe plot of data of LeClair and McConkey (1993) for production of
\( \text{O}(^1\text{S}) \) from \( \text{N}_2\text{O} \). The straight line was obtained from a linear regression analysis of
the data above 500 eV. Its X intercept is 71.2 ± 11.9 eV. From LeClair (1993)

Insert Figure 14 here.

\( f \) for this transition has been measured by Zelikoff et al. (1953) and by Rabalais et
al. (1971) using traditional optical absorption techniques. In addition, Heubner et
al., (1975) using electron scattering techniques, obtained a value in close agreement
with the optical absorption results. Adopting an average value for \( f \) of 0.360±0.007
in conjunction with their measured value of $C_i$ of $0.048 \pm 0.008$ allowed LeClair and McConkey to put their relative excitation function on an absolute scale. The peak cross section, at around 45 eV, was found to be $2.25 \times 10^{-17}$ cm$^2$ dropping to $0.65 \times 10^{-17}$ cm$^2$ at 1000 eV. The accuracy of these numbers was limited by the accuracy of the measured $f$-value (~3%) and by the accuracy of the extrapolation procedure to obtain $C_i$. However the sensitivity of the cross section to inaccuracy in $C_i$ is reduced because $C_i$ appears in the ln term. For example, the 16% uncertainty in establishing $C_i$ results in an uncertainty of only 8% in $\sigma$. Hence the cross section values given are uncertain at the 10% level or less.

This application of the Bethe-Bom calibration technique seems to be particularly advantageous because it is not complicated by polarization effects which normally have to be considered when optical emission from an excited state is being monitored. Cascade from higher excited states also does not seem to be a problem. If this was occurring it would almost certainly produce changes in the TOF distributions as the incident electron energy was varied.

Once the absolute cross section for production of O($^1S$) from N$_2$O had been established, it was a relatively simple procedure to obtain absolute data for production of the species from other targets using a relative flow technique [see e.g. LeClair and McConkey(1994)]. In this, signals from the target species to be calibrated are compared with those from N$_2$O under identical experimental conditions - target gas density, electron beam current, excitation energy etc. As an example, LeClair and McConkey (1993) estimated errors of 15% in this procedure when O$_2$ was being considered. Combining this with the 10% error in the N$_2$O cross section resulted in an overall error of some 18%.

When absolute calibration of CO$_2$ data was being considered, the fact that the masses of CO$_2$ and N$_2$O were the same meant that the relative flow technique was simplified. Because of this fact the gas beam profiles and densities could be considered the same to a very good approximation. LeClair and McConkey (1994) tested this for source driving pressures ranging over an order of magnitude from 1-10 torr and found that relative O($^1S$) production rates stayed constant in this pressure regime. This also strongly suggests that any quenching of the metastable species by background gas between the interaction region and the cold finger is negligible in this situation.

A very helpful factor in monitoring the variation of source densities comes from the fact that very often the prompt photons being detected come from excited atoms following dissociative excitation of the target molecule. Such photons will
not be subject to self absorption by background species, which will be predominantly unexcited molecules, and because they are unpolarized they will not introduce any spurious effects caused by any polarization sensitivity of the detector. Thus prompt photon count rates can often be used to track variations in target gas densities as source driving pressures are changed or to decide when molecular flow conditions apply (i.e. when target densities are directly proportional to source driving pressure).

**IV. B. Calibration of O(\textsuperscript{1}D) production.**

With O(\textsuperscript{1}S) one can use the fact that the oscillator strength for production of this species from N\textsubscript{2}O is well known and so N\textsubscript{2}O can be used as a secondary standard allowing other gases to be calibrated using a relative flow technique. With O(\textsuperscript{1}D) we might anticipate that another target gas, e.g. O\textsubscript{2}, could be used to provide a secondary standard. The following points would support this.

Most of the production of O(\textsuperscript{1}D) from O\textsubscript{2} comes from the B \textsuperscript{3}\Sigma_u^- state. This is the state which gives rise to the Schumann-Runge continuum in optical absorption. It is very well quantified and its oscillator strength is well known. Thus we could use it to do a Bethe-Born type calibration as was done originally for O(\textsuperscript{1}S) production from N\textsubscript{2}O, LeClair and McConkey (1993).

Having put the O\textsubscript{2} data on an absolute scale, a standard relative flow technique could then be used to calibrate other oxygen containing molecules, CO\textsubscript{2}, CO etc. In the case of some targets, e.g. CO\textsubscript{2}, we note that data is available for the absolute emission cross sections at 100 eV of the 3p \textsuperscript{5}P \rightarrow 3s \textsuperscript{5}S and 3p \textsuperscript{3}P \rightarrow 3s \textsuperscript{3}S transitions of atomic oxygen at 777.4 and 844.6 nm respectively, (Zipf, 1984). These are the lines which are transmitted by our red filter when measuring O(\textsuperscript{1}D).

These lines are also emitted in the dissociative excitation of O\textsubscript{2} and we note that there is good (15%) agreement in the 100 eV cross sections between measurements of Zipf (1984) and Schulman et al (1985). This adds an extra dimension to the relative flow measurements since comparison of the prompt photon signals from O\textsubscript{2} and CO\textsubscript{2} allows a very useful check on relative target gas densities as the relative flow technique is applied.
Although this calibration method is good in principle, in practice it is unusable with our present experimental set up. We found that when the temperature of the cold finger is reduced to <20K, which is necessary to establish a Ne matrix, oxygen acts as a very efficient spoiler of the matrix sensitivity quickly reducing observed signals to zero. No such problems were observed in the original measurements of O(1S) from O₂ where a much higher temperature, ~70K, was used with a Xe matrix and where less deposition of oxygen on the cold finger would occur. We note that Yurtaeva et al (1990) found that increase of oxygen content in their samples above a concentration of about 3 x 10⁻²% had the effect of attenuating their luminiscence intensities rapidly. Hence much better differential pumping would be necessary than is currently available with our apparatus if O(1D) from O₂ is to be studied.

IV. C. Calibration of the electron energy scale.

This calibration is straight forward if the prompt photons which are passed by the filter can be positively identified. Thus in the case of O(1S) production from CO, LeClair et al (1994) used the (4,0) Asundi band at 859.2 nm with an onset energy of 7.45 eV to fix the energy scale. As another example, Kedzierski et al (2013), in their study of the production of O(1D) from CO₂, used the the 3p ⁵P → 3s ⁵S and 3p ³P → 3s ³S transitions of atomic oxygen at 777.4 and 844.6 nm respectively where the mean minimum energy required to dissociatively excite these lines is 16.29 eV. In their study of the beak up of D₂O to yield O(1S) Derbyshire et al (1997) used the Balmer-α threshold at 18.25 eV to fix the incident electron energy scale.

Even when the electron energy scale has been established, it is sometimes difficult to fix the onset of a particular dissociation process for the following reasons:

1. Atomic and molecular fragments produced by the dissociative excitation of a molecule can possess significant kinetic energy due to the repulsive potential surfaces of the parent molecule involved. By the conservation of energy, the range of kinetic energies for the fragments causes a corresponding spread in the threshold energies. Therefore, the thresholds in electron-molecule collisions often have an extended concave upward slope, which makes determining the threshold energy less straightforward.
2. If a molecular fragment is produced, then excitation to the different vibrational-rotational levels can further increase the curvature. One may define the threshold energy as the measured energy at the bottom of the curve where the signal first appears (appearance energy), which corresponds to the minimum kinetic and ro-vibrational energy. The threshold energies so defined will be closer to the values calculated using the NIST Chemistry WebBook which are not intended to account for the kinetic or ro-vibrational energies of fragments. Alternatively, one may extrapolate the linear portion of the excitation function above the curved region down to zero cross section, but then the resulting threshold energies can include large kinetic energies.

3. A further blurring of the appearance energy occurs because of the finite energy resolution of the electron gun. Typically for an unselected gun with a directly heated filament the full-width half maximum (FWHM) of the electron energy resolution is approximately 1 eV.

4. Different processes, with onset energies that cannot be resolved, may be occurring.

V. \( \text{O}^{(1S)} \) Measurements.

To date \( \text{O}^{(1S)} \) production from the following molecules has been studied – \( \text{O}_2, \text{CO}, \text{NO}, \text{N}_2\text{O}, \text{H}_2\text{O}, \text{D}_2\text{O}, \text{CO}_2, \text{and SO}_2 \), [LeClair and McConkey (1993, 1994), LeClair et al, (1992, 1994, 1996), Derbyshire et al, (1997), Kedzierski et al (1998, 2000, 2010]. Much of the data has been discussed by McConkey et al (2008). Data sets for production of \( \text{O}^{(1S)} \) from the various target molecules in the energy range up to 1 keV have been collected in Table I.

In the following sections we have chosen results which demonstrate the usefulness of the detector and highlight the possibilities and advantages of using it. For a more detailed discussion the reader is referred to the original publications

V. A. \( \text{O}_2 \)

Figure 15 gives a comparison between the early TOF data of Kiefl et al (1983) and the later work of LeClair and McConkey (1993). The two data sets are very similar when allowance is made for the longer flight path in the earlier work. As mentioned earlier, the basic difference between the experimental set-ups is that Kiefl et al used a different (blue/green) filter to observe radiation from the solid Xe surface. Clearly both groups are observing the same dissociation process.
It is possible to conclude that the signal is due only to O(^1S) and not to any other atomic or molecular metastable particle. O(^1D), O(^3S), O(Rydberg) and O_2(M) all have TOF spectra which are distinctly different from the data of Figure 15.

Figure 15. Comparison of TOF for O(^1S) fragments following electron impact dissociation of O_2. The upper picture is taken from Kiefl et al (1983) and refers to 130 eV impact energy whereas the lower picture is from LeClair and McConkey (1993) and shows four different impact energies. The difference in the position of the main peak is due to the somewhat longer (20%) flight path in the earlier work.

Insert Figure 15 here.
Released kinetic energy obtained from the LeClair and McConkey (1993) data in Figure 15. Each data set has been normalized to unity at its maximum. Note that the extra noise seen at small values of released kinetic energy is due to the magnification of the noise by the $t^3$ factor in Eq 1.

Using the method discussed in Section IIIA we can transform the TOF data, Figure 15 to kinetic energy data and hence get the total released kinetic energy (RKE) since the undetected O atom will have identical kinetic energy. This is shown in Figure 16. Inspection of Figures 15 and 16 reveals the presence of three features. The primary feature is the sharp peak at 41 µs. A second less intense feature can be seen as a shoulder on the short TOF side of the main peak. It arises at electron energies greater than 30 eV. The third feature can be seen more clearly in the RKE spectra at around 5 eV. The RKE spectra reveal that a minimum of 4 eV is released in the dissociation process. Thus dissociation must be taking place via purely repulsive states in O$_2$.

Using the work of Stone et al (1975, 1976), Borst and Zipf (1971), Freund (1971), Mason and Newell (1990), Kiefl et al (1983), or have thresholds which are distinctly different from the 14 eV threshold observed in the present work.

Insert Figure 16 here.

Insert Figure 17 here.

Figure 17. Excitation probability for O($^1S$) production from O$_2$. From LeClair and McConkey (1993).
The measured threshold for production of metastable fragments was $14.0 \pm 0.5$ eV strongly suggesting that one process being observed was:

\[
e + O_2( X^3\Sigma_g^-) \rightarrow (O_2)^* \rightarrow O(^3P) + O(^1S) + e'\]  

(3)

The calculated threshold for this process given a kinetic energy release of 4 eV is 13.3 eV. A clue to the identity of the $(O_2)^*$ responsible is obtained from a measurement of the $O(^1S)$ excitation probability as a function of electron energy. This is shown in Figure 17. The shape is typical of optically allowed transitions and hence, since the ground state of $O_2$ is $3\Sigma_g^-$, the parent excited state must be of triplet and ungerade character. Singlet states, such as those dissociating to two $O(^1S)$ atoms or $O(^1S) + O(^1D)$, can be excluded because their excitation would require a spin flip with a characteristic sharply peaked excitation function with a maximum close to threshold. Of the four possible triplet states which can result from $O(^3P) + O(^1S)$ namely $3\Sigma_u^-, 5\Pi_u, 4\Sigma_g^-$ and $5\Pi_g$, [Saxon and Liu, (1977)], the first two are likely contributors to the overall $O(^1S)$ production but not near threshold as they cross the outer edge of the Franck-Condon region close to 19 eV some 4 eV higher than we observe experimentally.
Figure 18. Potential energy diagram for a few of the lower lying states of O$_2$ showing the approximate position of the repulsive curve (dashed) responsible for O($^1$S) production in the near threshold region. Solid lines are taken from the work of Gilmore (1965), Saxon and Liu (1977), Guberman (1983) and Guberman and Guisti-Suzor (1991). Note that the $^5\Sigma_u^-$ is not shown as it lies very close to $^3\Sigma_u^-$. Insert Figure 18 here.

The most likely candidate to explain the dominant 42 µs TOF feature is the $^5\Pi_g$ state which, although gerade in nature and thus optically forbidden from the ground state, lies very close to our experimentally determined repulsive curve. The differences between the two curves might be due to possible thermalization delays in the Xe matrix. If a delay of a few microseconds occurred between arrival of O($^1$S) at the Xe surface and photon emission, this could explain the small differences (~1eV) between the experimental curve and the calculated one.

This ability to distinguish between many possible alternatives is a nice example of how a complicated dissociative pattern can be greatly simplified when a very selective detector such as the rare gas matrix is available.
**Figure 19.** Released kinetic energy distribution obtained from the TOF spectrum (Figure 10). The dashed curve represents the theoretical RKE distribution if there was no vibrational excitation of the N\(_2\) fragment. The solid curve represents the fit to the data using the N\(_2\) vibrational population shown in the insert. From LeClair (1993).

Insert Figure 19 here.

**V.B N\(_2\)O.**

In addition to providing an excellent procedure for putting the data for O\(^{(1)S}\) production on an absolute basis, as discussed in Section IV, use of N\(_2\)O targets with the very simple dissociation pattern obtained when producing O\(^{(1)S}\) allows very specific information about the dissociation products to be obtained. Knowing that the dissociation is defined by:

\[
e + \text{N}_2\text{O}(X^1\Sigma^+) \rightarrow \text{N}_2\text{O}(D^1\Sigma^+) \rightarrow \text{N}_2(X,v) + \text{O}^{(1)S} + e' \quad (4)
\]

we can extract information about the vibrational distribution of N\(_2\)(X,v). This we do as follows. First we transform the TOF data, Figure 10, to released kinetic energy (RKE) data as discussed in Section III. This is shown in Figure 19. The shape of the N\(_2\)O D state potential energy surface can be deduced from the UV absorption spectrum [Zelikoff et al, (1953), Rabalais et al, (1971)]. From this the RKE distribution, which would be obtained if the N\(_2\) remained in its ground
vibrational state, can be calculated. This can be represented by a Gaussian function and is shown by the dashed curve, Figure 19. Using many of these Gaussian functions shifted towards lower energies by increments equal to the vibrational energy levels of N₂ and applying a weighting factor to each one, a qualitative fit to the RKE data can be obtained. This is shown by the solid line, Figure 19. The weighting factors used are shown in the inset and represent the distribution of vibrational states of the undetected N₂ fragment. We note that the results are similar to those of Stone et al (1976) in their study of photon induced dissociation of N₂O.

V.C. CO₂

Study of O(^1S) production from CO₂ [LeClair and McConkey, (1994)] revealed that this interaction was much more complicated than the one with N₂O with at least six channels contributing to the observed TOF spectra. Nevertheless it was possible to identify and quantify some of the channels from appearance potential and other measurements. An interesting feature of this work was the discovery that the Xe matrix was also sensitive to CO(a^3Π) metastable molecules. This is discussed in Section VIII.

V.D. CO

O(^1S) production from CO was found to be as complicated as from CO₂ with five different channels contributing. Tentative identification of two of these channels was possible. The total cross section for O(^1S) production at 100 eV was found to be one quarter that for production from O₂ at the same energy. Production of CO(a^3Π) from a CO parent will be discussed in Section VIII.

V.E. NO

O(^1S) production from NO was found to be very weak [LeClair et al (1996)]. No absolute data are shown in Table I but an approximate comparison with CO suggested a production cross section of <10^{-19} cm² at 100 eV. Two channels contributed to the observed TOF spectra with RKEs in the ranges 1.5-6 eV and 2-16 eV respectively.
V.F. H₂O, D₂O

Dissociation of water with production of O(^1S), [Derbyshire et al (1997), Kedzierski et al (1998)], was another nice example where the selectivity and sensitivity of the detector allowed a very selective probe of the multitude of possible dissociation surfaces along which the molecule may fragment. A single broad TOF curve was obtained with a long tail to larger flight times. A maximum occurred at a flight time of about 110 (130) µs for D₂O and H₂O respectively, Figure 20.

**Figure 20.** TOF spectra for O(^1S) fragments produced by 90 eV electron impact on H₂O and D₂O. Zero time corresponds to the center of the 20µs wide electron pulse. The spectra have been normalized so that the metastable peaks have the same height. From Kedzierski et al (1998). Insert Figure 20 here.

At higher (lower) incident electron energies leading the TOF distribution is shifted slightly to shorter (longer) flight times and the full width at half maximum (FWHM) of the peak narrows (broadens) by a few percent. The energetics of the break-up near threshold allow the dominant excitation-repulsion mechanism there to be identified as

\[
e + \text{H}_2\text{O}(\text{X^1A}_1) \rightarrow \text{H}_2\text{O}^*(\text{^1A}_1) \rightarrow \text{O}^{(^1S)} + 2\text{H}^{(^2S)} + e' \quad (5)
\]
From the shape of the production cross section as a function of electron energy it is clear that optically allowed, i.e. singlet, repulsive states dominate the excitation. O(\(^1\)S) production was shown to be a non negligible (~8%) fraction of all dissociations leading to production of excited neutral fragments.

**V.G. SO\(_2\)**

Measurements here [Kedzierski et al, (2000)] revealed that at least three processes contributed to O(\(^1\)S) production. One of these produced high-energy fragments originating from a steeply repulsive surface lying more than 50 eV higher in energy in the Franck-Condon region than the ground state. The other two dominate O(\(^1\)S) production at lower energies. They involve two-body breakup with either ground or excited state SO molecular partners.

**VI. O(\(^1\)D) Measurements**

O(\(^1\)D) is not detectable using solid matrices of the heavier rare gases, xenon krypton and argon, because any excimers produced under these circumstances undergo rapid non-radiative transitions to the ground state. However when Ne is used as the host matrix a different situation applies. This had first been noticed in early work where fluorescence following VUV irradiation of solid Ne containing traces of O\(_2\), N\(_2\)O or CO\(_2\) was studied,[Walker et al (1981), Maillard et al (1982, 1983), Fournier et al (1982)]. They observed the spin-forbidden (\(^1\)D – \(^3\)P) emission near 630nm (see Figure 1) in addition to the auroral green (\(^1\)S-\(^1\)D) feature. Later work by Belov et al (2000) using 2 keV electron bombardment of Ne crystals containing a trace of O\(_2\) also demonstrated the (\(^1\)D – \(^3\)P) fluorescence. This suggested that a Ne matrix could be used to detect \(^1\)D atoms and this was in fact shown to be the case by Kedzierski et al (2010, 2013) using N\(_2\)O and CO\(_2\) targets. In contrast to the work with the heavier rare gases, where the excimer emissions were broad and shifted in wavelength from the atomic line, the Ne features were narrow and unshifted. Because Ne solidifies at a lower temperature than the other rare gases it was necessary to cool the detector to less than 30K in order to obtain a workable surface. The efficiency for O(\(^1\)S) detection using Ne was the lowest of all the rare gases (see Figure 12) and, when using Ne, the efficiency for O(\(^1\)D) detection was much lower than for O(\(^1\)S). Thus data accumulation times for O(\(^1\)D)
detection tended to be very long to obtain reasonable statistical accuracy. It has not yet been possible to study the formation of \( \text{O}^{(1)}\text{D} \) in the break up of \( \text{O}_2 \), presumably because of deterioration of the sensitivity of the detector surface at these low temperatures caused by background \( \text{O}_2 \) \cite{Yurtaeva et al (1990)}. Figure 21 shows a typical example of an \( \text{O}^{(1)}\text{D} \) TOF spectrum from \( \text{N}_2\text{O} \) and shows the \( \text{O}^{(1)}\text{S} \) spectrum as well for comparison. A very similar \( \text{O}^{(1)}\text{D} \) TOF spectrum was obtained with \( \text{CO}_2 \) targets.

![Figure 21. \( \text{O}^{(1)}\text{S} \) and \( \text{O}^{(1)}\text{D} \) TOF data obtained using 100 eV electron impact on a \( \text{N}_2\text{O} \) target. The e-beam pulse width was 25\( \mu \)s and the target driving pressure was 5 torr. Note that the prompt photon peaks at zero time have been suppressed for the sake of clarity. Green and red filters were used to obtain the two different data sets. Data-taking time for \( \text{O}^{(1)}\text{D} \) was much longer than for \( \text{O}^{(1)}\text{S} \) so the two data sets can not be compared directly. From Kedzierski et al (2010).](image)

When converted to a FKE spectrum the data show a single broad feature peaking at at a few tenths of an eV and having a tail extending to 2 eV or higher. Data for the production of \( \text{O}^{(1)}\text{D} \) as a function of exciting electron energy are shown in Figure 22 for a \( \text{CO}_2 \) target. Due to the low signal levels we note that the
statistical quality of the data is poor. Two data taking modes were used to obtain the data as noted in the figure caption.

Figure 22. Excitation probability for $\text{O}(^1D)$ production from CO$_2$ as a function of impact electron energy. The dots represent data where the impact electron energy was ramped. The solid squares indicate data taken at particular impact energies. The solid curves indicate a possible breakdown of the plot into its individual optically allowed components. A representative error bar has been included for the 100 eV datum point. From Kedzierski et al (2013).

Some comments are relevant regarding Figure 22. First, the measured threshold of 8±1 eV is consistent with photon impact measurements [Stolow and Lee (1993), Miller et al (1992), Zhu and Gordon (1990), Slanger and Black (1971, 1978)] and demonstrates the opening of the optically-allowed fragmentation pathway:

$$e + \text{CO}_2(^1\Sigma_g^+) \rightarrow \text{CO}(^1\Sigma_g^+) + \text{O}^1D_2$$

Second a Bethe-Born plot of the data in Figure 22 displays a positive slope at the highest energies indicating that the excitation is dominated by optically allowed
transitions in that energy region also [see Inokuti (1971)]. The solid lines in Figure 22 indicate an attempt to fit the observed data assuming that two optically allowed excitations are dominant.

VII. Sulfur Measurements.

Since S is isoelectronic with O it has a similar ground-state configuration with similar \(^1\)S and \(^1\)D metastable levels. Thus it is reasonable to expect the rare-gas matrix detector might be effective in detecting these S metastables as well. OCS should be a good target molecule to test this suggestion as it is known from photon impact studies that S(\(^1\)S) is produced with high efficiency following absorption at wavelengths shorter than 170 nm, [Black et al (1975, 1980), Black and Sharpless (1979), Taylor et al (1980), Strauss et al (1989), Itakura et al (2000)]. In addition studies of photo-dissociation of OCS in host liquids and solids revealed the presence of excimer band emission close to the wavelength of the atomic S (\(^1\)S – \(^1\)D) transition at 772.7 nm, [Black et al (1980), Brom and Lepak (1976), Taylor et al (1980)]. In particular, Taylor and Walker (1979a,b) demonstrated that the wavelength of the photoluminescence moves progressively to the red as the rare gas host matrix is changed from Ar to Kr to Xe. In Xe it is peaked at 809 nm. The lifetime of the XeS emission was measured to be between 2 and 3.5 \(\mu\)s.

Using the same experimental set-up as for O(\(^1\)S) studies with a Xe matrix on the cold finger, we monitored the spectrum of radiation observed when pulsed excitation of an OCS beam occurs using 100 eV electrons. The result is shown in Figure 23 which also shows the prompt photon spectrum measured in coincidence with the electron pulses. As is evident we observe a broad feature in the near infra red peaked at 810 nm in very close agreement with Taylor and Walker’s work. We note that the feature occurs at a different (longer) wavelength than the equivalent emission from XeO*. We were not able to detect any evidence for O(\(^1\)S) excitation in electron-OCS collisions.
Figure 23. Low resolution spectra taken at 100 eV electron impact energy. Upper spectrum shows direct fluorescence from the interaction region when the e-beam is pulsed on. Lower spectrum shows emission from the cold finger when the e-beam is off. From Kedzierski et al (2001). Insert Figure 23 here.

The prompt photon spectrum, Figure 23, consisted of various band systems of CO and CO$^+$ together with the strong atomic oxygen lies at 777 and 844 nm. Atomic sulfur emissions at 566 and 630 nm are also present.

Figure 24. TOF spectrum for metastable S($^1$S) fragments produced by 100 eV electron impact on OCS. Zero time corresponds to the centre of the electron pulse. From Kedzierski et al (2001) Insert Figure 24 here.
Figure 24 shows TOF data taken at an incident energy of 100 eV though an essentially identical data set is obtained for all impact energies. The large peak at time zero is due to photons which are produced in the interaction region during the electron beam pulse. A single broad peak is then observed with a maximum at arrival times of 125 μs as the S(^1S) atoms arrive at the xenon surface. Thermalization times at the surface are assumed to be negligible compared to transit times from the interaction region. This is consistent with our findings for O(^1S). The fact that this peak is independent of the incident electron energy is a strong indication that a single S(^1S) production process is dominating the dissociation into this fragment.

![Figure 24](image)

Figure 25. S(^1S) fragment kinetic energy spectrum obtained from the data shown in Figure 24. Some smoothing has been applied for clarity. From Kedzierski et al (2001).

Insert Figure 25 here.

Converting the TOF data of Figure 24 yields the kinetic energy spectrum shown in Figure 25. The spectrum is truncated at energies below 0.2 eV because of the poor quality of the data at these low energies. A symmetric peak is observed with a maximum at 0.65 eV and with a FWHM of 0.5 eV. This peak in the S(^1S) fragment kinetic energy translates into a total released kinetic energy of 1.4 eV based on two fragment break-up and conservation of momentum considerations. Assuming that the original transition in the OCS molecule was from the ground ^1Γ+ to the 2 ^1Γ+ excited state where the most probable excitation energy is 8.13 eV, [152.3 nm, (Rabalais et al, 1971)], and that 5.87 eV is expended in dissociating OCS into CO and S and in exciting S to the ^1S electronic level, [see Strauss et al, (1989)], means
that 0.86 eV is available for vibrational and rotational excitation of the CO fragment. This suggests two or three quanta of vibrational excitation of the CO.

A number of photodissociation studies of OCS have been carried out, using 157 nm radiation from an F2 eximer laser, to make direct measurements of the S(^1S) kinetic energy or of the CO vibrational distribution. Those by Strauss et al (1989) indicated that only vibrational levels v=0,1,2 and 3 were significantly populated. More recent measurements by Itakura et al (2000) using Doppler profile analyses to obtain the S atom kinetic energies, are in substantial agreement with the work of Strauss et al (1989). Strauss et al concluded that about 84% of the energy available to the nuclear motion was allocated to the translational recoil motion of the fragments. This amounts to 1.3 eV in their case. The fact that this agrees well with our average value of 1.4 eV strongly supports our contention that this optically allowed 2^1Γ^+ repulsive state is the major avenue for dissociation via electron impact.

Additional evidence that S(^1S) production is predominantly via dipole allowed channels is obtained from Figure 26 which shows the cross section for production of this fragment as a function of impact electron energy. As is evident, the excitation function displays the characteristic broad shape with a maximum near 55 eV. The threshold energy on Figure 4 has been set to 8.1 eV based on the discussion above. The absolute cross section scale on Figure 26 has been established using the same method as was applied to N2O break-up by LeClair and McConkey(1993), [see Section IV A]. Assuming that the 2^1Γ^+ channel dominates we can normalise our measured cross section at high energy to the known optical oscillator strength (0.38, see Ondrey et al, 1983), for this transition, using a Bethe-Born procedure. The maximum cross section so obtained is 3.3x10^{-17} cm^2. with an error estimate of ~10%. This measurement may be compared with the maximum cross section for production of O(^1S) from N2O where a rather similar situation occurs with just one dominant, optically-allowed production channel. Here the appropriate oscillator strength was 0.36 and the maximum cross section was 2.25x10^{-17} cm^2 at an impact energy of 45 eV [see Table 1].
Figure 26. Absolute cross section for production of S\(^1\)S from OCS as a function of incident electron energy. The data have been normalized as discussed in the text. From Kedzierski et al (2001).

Insert Figure 26 here.


As for OCS the results suggested that the dissociation was dominated by a single, optically-allowed channel but the optical oscillator strength of the transition in the parent molecule was smaller than in OCS by at least a factor of ten. The dissociation partner to S\(^1\)S was demonstrated to be ground state CS.

**VIII. CO Measurements.**

While investigating the production of O\(^1\)S from CO\(_2\) targets, LeClair and McConkey (1964) discovered that their Xe matrix was also sensitive to CO\(^{a^3\Pi}\) metastable molecules. The fluorescence from the Xe layer was found to have an additional spectral component at 325 nm which arose from the formation of a XeCO\(^*\) excimer. (This might have been expected following the work of Bahrdt et al (1987) who irradiated solid rare gas:CO mixtures with synchrotron radiation and observed the resulting fluorescence).
Figure 27. Time of flight spectrum for CO(a³Π) fragments following 30 eV electron impact dissociation of CO₂. The small structure at 60 µs is due to O(^1S) (see text). From LeClair and McConkey (1994).

Insert Figure 27 here.

Figure 28. CO(a³Π) excitation probability from CO₂ as a function of electron energy. From LeClair and McConkey (1994).

Insert Figure 28 here.

A typical TOF curve is shown in Figure 27. The small feature at 60 µs is due to some fluorescence from XeO(^1S) decay being transmitted by the UG-11 filter used.
The shape did not change with electron beam energy suggesting that the excitation was dominated by a single process though structure on the excitation function, Figure 28, suggested that some other channels were providing minor contributions. In particular the initial sharp rise of the excitation function, Figure 28, is indicative of a spin flip occurring while the slow fall off to higher energies shows that optical allowed channels are dominating at these energies. Our relative excitation function for CO(\(a^3\Pi\)) production is in quite good agreement regarding the shape and the threshold energy with that of Freund (1971).

The CO(\(a^3\Pi\)) metastable particle, produced in electron collisions with CO\(_2\), emits the important Cameron bands, which are bright emission features in the atmospheres of both Mars and Venus. Apart from ourselves, a number of other workers [Clampitt and Newton (1969), Freund (1971), Misakian et al. (1975), Allcock and McConkey (1976), Barnett et al. (1992)] have studied the process, 

\[
e + \text{CO}_2(X \ 1\Sigma^+_g) \rightarrow \text{CO}(a^3\Pi) + O + e' \tag{7}
\]

using surface detectors that were sensitive to this species, while Erdman and Zipf (1983) studied the Cameron band fluorescence. Unfortunately lack of precise knowledge of such factors as detector sensitivity, particle lifetimes and hence in-flight decay probabilities, prevented reliable quantitative production cross sections being obtained.

CO(\(a^3\Pi\)) production from CO parent molecules was studied by LeClair et al (1994). They were able to study both O(\(^1\)S) and CO(\(a^3\Pi\)) production by using appropriate optical filters as for CO\(_2\) targets. In the CO study the target gas beam was directed towards the Xe matrix as the excited molecules possessed just thermal kinetic energies. An unstructured TOF curve was obtained with a shape which was modified by in-flight loss due to inter-molecule collisions. This caused the effective lifetime of the CO(\(a^3\Pi\)) metastable molecule to change significantly with the driving beam pressure. The measured excitation function is shown in Figure 29, where it is compared with data obtained by Furlong and Newell(1993) and calculations by Morgan and Tennyson (1993). The experimental data have been normalized at the peak to the absolute measurement of Erdman and Zipf (1983). Good agreement in the shape of the excitation function is obtained with the work of Ajello (1971) who measured Cameron band emissions directly. Furlong and
Newell’s function is much broader because they also observed contributions from higher lying (>10 eV) metastable states of CO. This is another example of the selectivity of the solid matrix detector.

![Graph](image)

**Figure 29.** Excitation of CO\((a^3\Pi)\) following electron impact on CO. Solid line, data of LeClair et al (1994); filled triangles, data of Furlong and Newell (1993); squares, calculations of Morgan and Tennyson (1993). The experimental data sets are normalized to the maximum cross section reported by Erdman and Zipf (1983). From LeClair et al (1994).

Insert Figure 29 here.

**IX. Future Possibilities.**

The rare gas matrix detectors have been shown to be sensitive to metastable atoms with an \(np^4\) outer electron configuration. Thus there is every reason to suppose that they will be sensitive to Se and Te and Po metastables in addition to O and S. Also it is quite possible that other atomic or molecular metastable states may be detectable. For example Crepin and Tramer (1992) show that radiation from the mercury 6p \(^3\)P\(_0\) metastable state is observable following UV irradiation of Hg atoms trapped in a rare gas matrix. This suggests that rare gas matrix detectors could be used to monitor the excitation of this species also. Detection of metastable charged fragments could also be a fruitful area of research, as demonstrated by the early work of Corr (1987) who used a Xe matrix to monitor O\(^+\)(\(^2\)P, \(^2\)D) production from O\(_2\). Use of a mass spectrometer in conjunction with the detector would be a
helpful addition. So far the detection scheme has been limited to fluorescence in the visible, near UV and near IR regions of the spectrum. Fluorescence outside this limited spectral region is also possible and there may well be situations where the advantages of this type of detection, e.g. the lifetime shortening and selectivity, could be exploited. The use of other matrices other than rare gas ones could also be explored. In this connection we have obtained promising results with solid nitrogen matrices which will be reported separately, [Kedzierski and McConkey (2014)].

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